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Ph Thesis

Summary

# Mechanism of the methyl group transfer reaction in selected cobalt and nickel complexes. Calculations by DFT method

Density functional theory (DFT/BP86) and the Polarizable Continuum Model (PCM/acetonitrile) for solvation have been applied to investigate the methyl transfer reaction from CH3I to Ni(PPh2CH2CH2SEt)2. Two different mechanisms were considered: SN2 and radical one. The reaction paths for both examined mechanism were determined, and the geometries of possible substrates and products were compared. On the basis of calculations the SN2 mechanism was confirmed.

Cobalamins, cobalt glyoximate complexes and nickel complexes with Triphos (bis(diphenylphosphinoethyl)phenylphosphine) and PPh2CH2CH2SEt ligands were studied with the DFT/BP86 method in connection with methyl transfer reactions.

Geometries, methyl binding energies and redox potentials were determined for the studied complexes. Three- and four coordinate structures were considered for nickel complex with PPh2CH2CH2SEt ligand, whereas four- and five-coordinate for its methyl derivative. On the basis of calculations, the possible mechanism of methyl transfer reaction between cobalt and nickel complexes was considered.

The calculations for methyl transfer reaction from $CH_3Co(dmgBF_2)_2py$ to $Ni(Trifos)PPh_3$ were performed. The DFT method with BP86 and PBE functional was used. Additionally calculations with disperdeion corrections were carried out. The calculations showed that the reaction mechanism is SN2. Before methyl transfer from cobalt to nickel, the phosphine ligand is dissociated. The reaction is slightly egzoenergetic after the solvent molecule is coordinated to nickel complex. The calculations with dispersion corrections show that association of the product molecules is possible. The best results are obtained for the VV10 dispersion correction. The D3-BJ corrections give very small reaction energy. The energy analysis shows that the reaction energy can be decribed as a function od ligand dissociation energy, methyl binding energy and redox potentials of cobalt and nickel complexes. One of the factiors which strongly influences the reaction energy is the nickel-phosphine binding energy. The BP86 method gives too small nickel-phosphine binding energy while BP86-D3BJ method gives too large nickel-phosphine binding energy. The calculations showed that the product molecules association and the solvent molecule coordination are very important in the reaction mechanism.